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YONKERS, NEW YORK

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FC

CEMENTED BORIDES CONTRACT

CONTRACT N6-ONR-256/1

SUMMARY PROGRESS REPORT

August 1, 1955 to July 31, 1956

CEMENTED BORIDES

CONTRACT N6-ONR-256/1

SUMMARY PROGRESS REPORT

FOR THE PERIOD

August 1, 1955 to July 31, 1956

TO

OFFICE OF NAVAL RESEARCH

DEPARTMENT OF THE NAVY

WASHINGTON 25, D. C.

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Borides of Rare Earth Metals. J. Amer. Chem. Soc., 78, 1800 (1956)  
 New Borides of Yttrium, Powder Metallurgy Bulletin, 7, 74, (1956)

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## I. INTRODUCTION

During the period covered by this Summary Progress Report (August 1, 1955 to July 31, 1956), the main emphasis has been on attempts to improve the impact strength of the otherwise satisfactory high temperature material Borolite IV (Cr<sub>2</sub>B + Cr-Mo alloy).

This investigation involved two major fields; one was the effect of microstructure upon physical properties with emphasis on effects relative to the impact strength, while the other was the substitution of cobalt or a cobalt-chrome alloy for all or part of the Cr-Mo alloy in Borolite IV.

Coating of Borolite IV has been postponed until the base material can show a sufficient impact strength to make possible the use of only a thin coat.

In basic research, the investigation of rare earth borides has been extended to the borides of the related metal, yttrium. A new type of rare-earth boride, believed to be a hexagonal diboride, but not as stable as the normal transition metal diborides, has been found.

A start was made on the low-boron end of the System Nb-B, with indications that the purity, especially as concerns the nitrogen content, would be critical.

In summary, work is being continued on an investigation of methods of improving the impact strength of Borolite IV compositions. With such an improvement, the other outstanding elevated temperature characteristics of this material--oxidation resistance, heat shock resistance, stress to rupture strength through at least 2000°F--could be properly utilized.

particle sizes in the order of 5 to 9 microns, as compared with 1 to 3 micron sizes in use for other hard-metal materials. It was therefore attempted to micronize the Cr-Mo alloy powder to produce a very fine particle size. This method worked well with  $\text{Cr}_2\text{B}$  and similar materials; it did not work at all with Cr-Mo. Even varying the conditions of micronizing, it was not possible in our setup to produce a Cr-Mo powder finer than 20 microns or a fine Borolite IV powder mixture. It is this apparent toughness of the Cr-Mo 80 - 20 alloy in any type of crushing or particle size reduction which gives rise to hopes that a means can be found to produce an impact resistant Borolite IV material.

## 2. Longer Time Milling

While micronizing did not work for the Cr-Mo alloy, it was possible to produce powders of workable fineness in the range of 8 microns by ball milling. Here also, however, the Cr-Mo alloy did not break down as easily or as completely as the  $\text{Cr}_2\text{B}$ .

This longer time milling did not produce any results in physical property improvement or microstructure change. The impact strengths, measured in the NACA drop impact tester, remained in the range of 1 - 1.5 inch pounds. Figure 1 shows a photomicrograph of normal Borolite IV 20/80 at a magnification of 400X. This picture shows the three basic constituents present in Borolite IV: the light colored liquid matrix, in the presence of which sintering takes place, which contains the shadowy, angular grains of  $\text{Cr}_2\text{B}$ , and the darker Cr-Mo phase, usually containing rod-shaped structures within each grain. The Cr-Mo grains and the liquid matrix "pools" occur somewhat in clusters; one object of this investigation was to produce a more uniform distribution, especially of the liquid matrix.



Figures 2 and 3, also at a magnification of 400X, show the microstructures obtained with longer milling times. Compared with the standard milling time of 24 hours, these powders were milled for 96 and 132 hours respectively, in the same milling setup. Each is a similar Borolite IV 20/80 powder (20 percent  $\text{Cr}_2\text{B}$  and 80 percent Cr-Mo alloy). Figure 2 shows a hot pressed specimen, which always gives a finer structure than the corresponding sintered bar, because of the shorter time at and near temperature. The structures are similar and in no case is there a thin film of liquid surrounding hard-metal grains, or any other different structure which might appear promising. These structures are the same type as shown in Figure 1. This is also reflected in the results of impact tests. Bars with approximately  $3/16$ " square cross section gave values of about 1 inch pound in the NACA drop impact test.

A chemical analysis of a batch of Borolite IV 20/80 milled for 136 hours indicated even a low pickup of iron from the mill. The iron content was 0.14%.

The longer milling times did, however, produce one different result. The finer powders so produced were, at first, much harder to handle. It was later found that it was necessary to take much more care in mixing the pressing lubricant and in cold pressing in order to produce sound pieces, and the die had to be in excellent shape. In the meantime, however, a method of getting around these difficulties in piece production was found, that of "warm pressing".

### 3. Warm-Pressing

In this "warm-pressing" procedure, the powder was heated to approximately 1300°C in a graphite die, in the hot press, to form a compact about 80% dense. This compact could then be sintered to full density to form a sound piece.

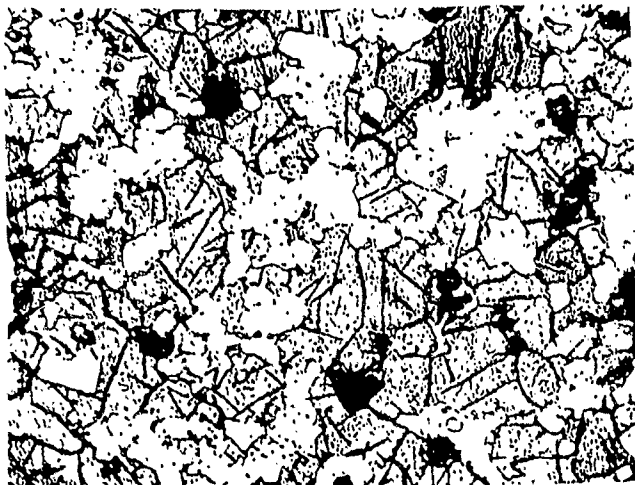


Fig. 1 Standard Borolite IV 20/80

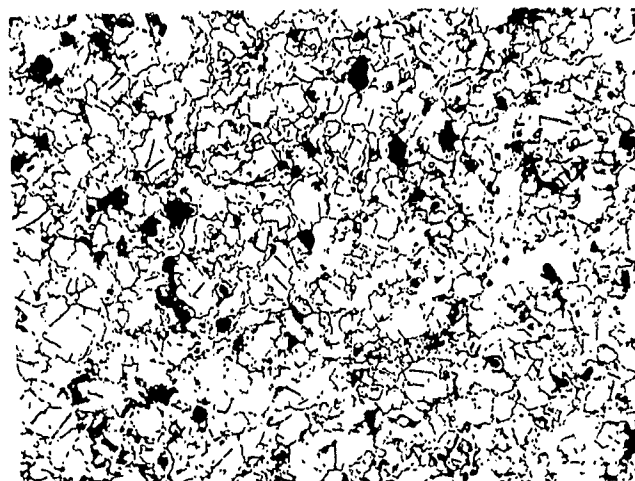


Fig. 2 Borolite IV 20/80  
Ball Milled 96 Hours

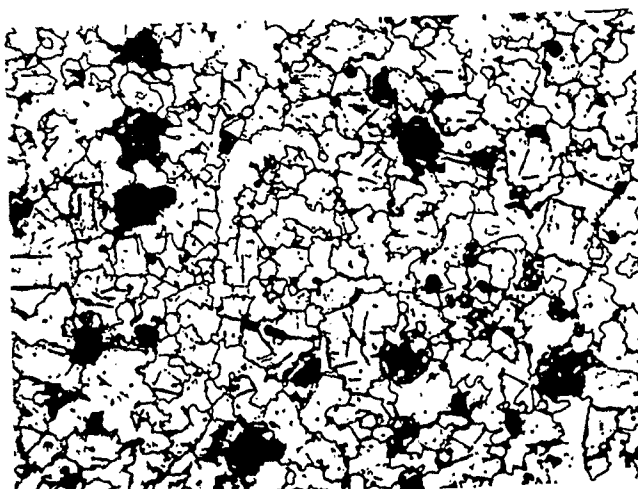


Fig. 3 Borolite IV 20/80  
Ball Milled 132 Hours

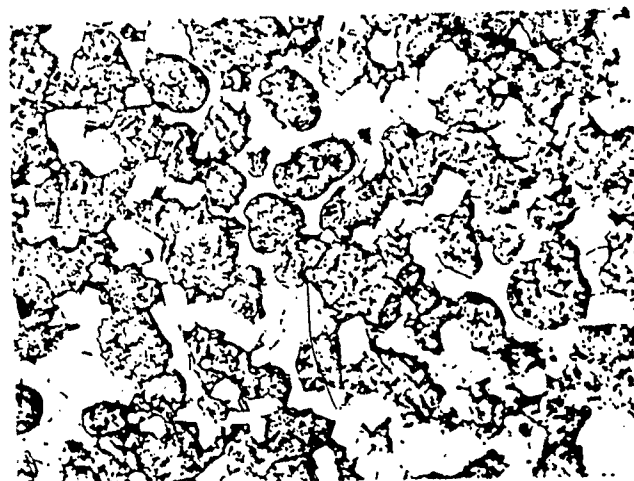


Fig. 4 Borolite IV 20/80  
18/1 Ball/Powder Ratio

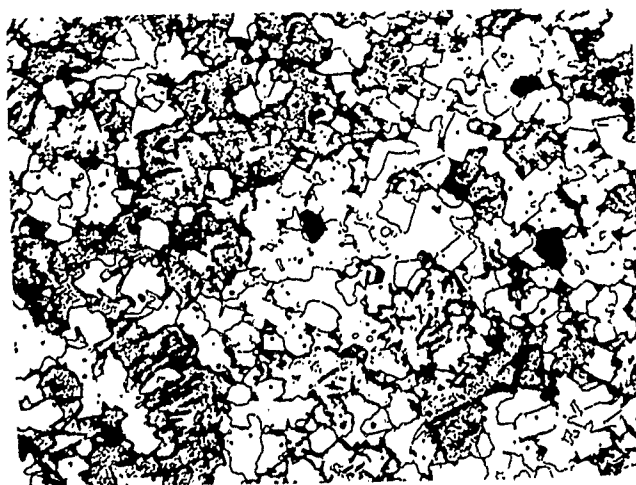


Fig. 5 Borolite IV 20/80  
Milled in Alcohol 24 Hours

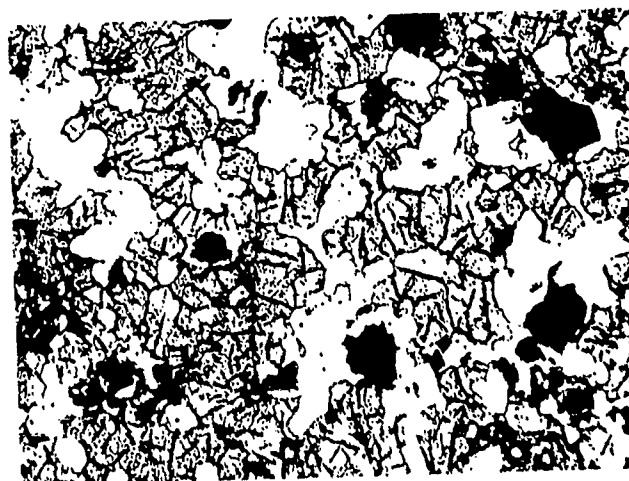


Fig. 6 Borolite IV 20/80  
Milled in Alcohol 96 Hours

This method was especially useful in making NACA impact bars, where the fine powders had caused considerable trouble.

#### 4. Large Ball to Powder Ratio

Two other attempts to control the particle size and distribution were made. One involved ball milling with a very high ball-to-powder ratio, 18 to 1 instead of the normal 6 to 1. A photomicrograph of an impact bar (NACA drop impact test 1.12 inch pounds) is shown in Figure 4, at 400X magnification. The structure is essentially the same as before; the apparent difference in the Cr-Mo grains is only an etching effect, although some of the Cr-Mo grains are more rounded than in the previous pictures. Unfortunately, this did not aid the impact strength. The boride grains are again confined to the liquid matrix.

#### 5. Milling in Alcohol

The other variation was to mill the Borolite IV powder in alcohol. Figures 5 and 6 show the cross sections of small bars pressed from such powders, each at 400X magnification. Figure 5 refers to a batch milled for 24 hours, Figure 6 to a batch milled for 96 hours, each Borolite IV 20/80. The sintered pieces were apparently identical. In Figure 5, some of the Cr-Mo grains are not etched as darkly as some others; otherwise, the photomicrographs are quite similar. Again, the liquid matrix forms into large lakes, not surrounding the Cr-Mo grains. The impact strengths were also unchanged.

### B. HEAT TREATMENT

Two types of heat treatment were applied to samples of Borolite IV and pure Cr-Mo. One involved heating the samples in air for a fairly long time at a temperature considerably under the sintering temperature; the other, heating for a much shorter time just under the sintering temperature.

### 1. Long Time, Low Temperature Heating

Samples of Cr-Mo 80/20 alloy and Borolite IV 5/95 were heated in air at 1200°C for 90 hours. Figure 7 shows the Cr-Mo piece, originally hot pressed, at 400X magnification. Some of the grains have grown, irregularly. There is little sign of any oxide--the darker spots are voids or carbon inclusions from the original hot pressing. Similarly, Figure 8, the Borolite IV 5/95, X400, shows a considerable grain growth. The slight elongation of the liquid pools is typical of the 5/95 composition, as is the apparent lack of separate Cr<sub>2</sub>B grains. These heat-treated samples were still brittle.

### 2. Higher Temperature Heat Treatment

The second type of heat treatment was a shorter heating at a temperature just below the sintering range. Treatments ranged from a few minutes at 1480°C to 16 hours at 1470°C, all in a hydrogen atmosphere. The only effect was a further grain growth.

### C. BOROLITE IV MELTS

A similar approach, also designed to influence the distribution of the Cr<sub>2</sub>B phase, was that of melting some samples of Borolite IV.

One bar of Borolite IV 20/80 was melted in an arc-melting setup, under a partial pressure of argon. The photomicrograph of this sample, effectively quenched from a melt, is shown in Figure 9. The grain outlines are not very distinct in some cases, though the boride particles appear to be very small. A small sample ground from the melted button was still brittle. There was some segregation of a darker material, probably impurities, leading to the idea that it might be possible either to purify Borolite IV in vacuum, or to make the raw materials directly in a vacuum furnace, or under a partial pressure of an inert gas.

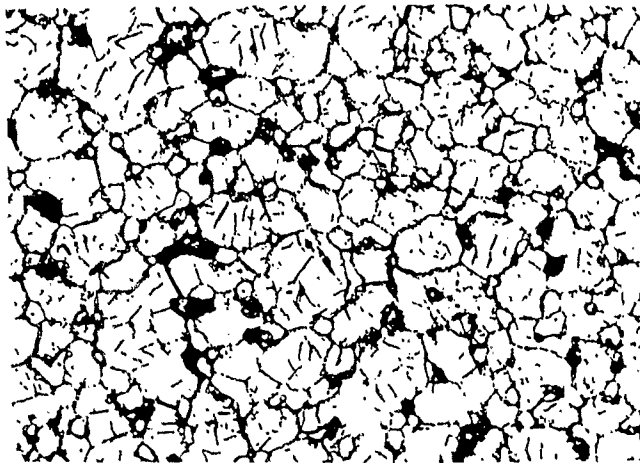


Fig. 7 Cr-Mo 80/20  
Heated in Air  
1200°C 88 Hours



Fig. 8 Borolite IV 5/95  
Heated in Air  
1200°C 88 Hours



Fig. 9 Borolite IV 20/80  
Arc Melted

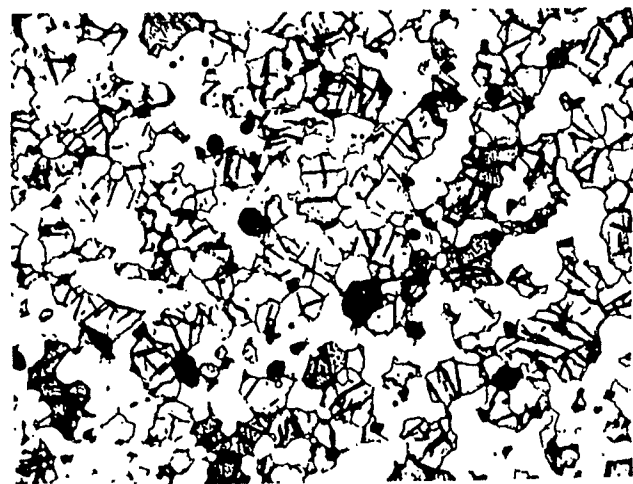


Fig. 10 Borolite IV 20/80  
Melted in High Frequency  
Setup

Another Borolite IV 20/80 sample, this one consisting of several old transverse rupture and impact bars, was melted in a ceramic container in a high frequency setup, under hydrogen. Here, the cooling was much slower than in the arc melting apparatus. This melt was crushed and processed in similar fashion to original raw materials. A photomicrograph of such a sintered piece is shown in Figure 10. An analysis of this batch showed low oxygen and nitrogen contents, and a loss of boron, from the 2% theoretical to 1.25%. An X-ray pattern of the powder indicated only Cr-Mo, but Figure 10 shows some of the angular boride grains, probably too few in number to show up in the X-ray pattern. The grain outlines are quite sharp and there appears to be a considerable amount of the liquid phase; however, the impact strength is still in the same low range (1 to 1.5 inch pounds in the NACA drop impact test, 3/16" square cross-section).

#### D. CONTROLLED IMPURITY ADDITIONS

Another means of trying to change the microstructure of Borolite IV to a form with more impact resistance was the addition of small amounts of controlled "impurities".

There were several possibilities. Solution of the "impurity" at the sintering temperature in the binder material could cause a change in the wetting character and, thereby, the distribution of the liquid. A better wetting of the individual hard particles by the liquid binder could produce a more uniform distribution of the constituents. It was also possible that certain of the additions would segregate impurities.

Borolite IV 20/80 was selected as the starting material, with nine "impurities" to be added, each in the amount of 2% by weight. The additions were Cu, Ni, Co, Nb, Mn, Al, Ti, Cr<sub>2</sub>O<sub>3</sub>, Fe. Titanium was added as the hydride; the others, except, of course, for Cr<sub>2</sub>O<sub>3</sub>, were added as metal powders.

The manufacture of samples from these batches ran into some difficulties; here too, warm pressing was of help in making sound test specimens.

One of the nine additions, that of Al, was rapidly dropped. It was not possible to make a test specimen with any reasonable strength or hardness; in fact, it was never possible to make an impact specimen.

Two other additions were also soon dropped. The addition of  $\text{Cr}_2\text{O}_3$  produced no advantages, and only resulted in reducing the strength of the Borolite IV and making it still more brittle. Hot bend tests, 18 hours at  $1000^\circ\text{C}$  with a load of 40,000 psi, could not be conducted on this material--the samples broke. NACA drop impact tests produced values of 0.2 inch pounds. Similarly, iron was dropped as an addition agent because of the low strength, low density and extreme irregularity of all pieces.

The other additions, Ni, Cu, Ti, Mn, Co and Nb, produced results similar to those with straight Borolite IV 20/80. In each case, the impact strength in the NACA drop impact test, was 0.5 to 1.7 inch pounds with a bar of approximately  $3/16$ " square cross section. Photomicrographs of four of these additions are shown in Figures 11 through 14. Figure 11 shows the 2%  $\text{Cr}_2\text{O}_3$  addition. The dark sections are either the  $\text{Cr}_2\text{O}_3$  or filled-in pores in the sample. Figure 12 shows a sample with 2% Ni. Though outlines are not absolutely clear, the general picture is the same as that seen previously. Figure 13 shows a 2% Cu sample, also quite similar. Though these two bars indicated close to theoretical density, the photomicrographs indicate quite some porosity. This may also be due to material being ripped out in polishing.

Figure 14 is a sample with a 2%  $\text{TiH}_2$  addition. This bar was sintered at a somewhat higher temperature than any of the others,  $1550^\circ\text{C}$  as compared to  $1500^\circ\text{C}$ . The liquid seems to contain much larger angular pieces of boride

than are normally seen in Borolite IV photomicrographs. Further experiments with this particular material definitely seem to be indicated.

Other than the work on the cobalt binder to be mentioned in the next section, no attempts have yet been made to add more than 2% of these "impurities" to Borolite IV. It is possible that effects upon the microstructure would only be visible with larger additions.

Borolite IV is always sintered in the presence of a liquid phase; in a composition 20 Cr<sub>2</sub>B - 80 Cr/Mo binder, the hardmetal phase is completely dissolved during the sintering and precipitates out of the liquid in cooling. This follows from the Cr-B diagram (see last Summary Report, July 31, 1955, pg. 82), as the boron content is less than that which corresponds to the composition of the Cr/Cr<sub>2</sub>B eutectic. It might be advisable for future experiments to extend these "wetting" studies to a boron range which would preserve a Cr<sub>2</sub>B skeleton during sintering, i.e. to a boron content of about 5%, corresponding to 50 - 60% Cr<sub>2</sub>B. Even though previous experience indicated excessive brittleness of these compositions, such a study may be worthwhile, as-- with different wetting properties of the binder material--these materials may change considerably in their behavior.

#### E. COBALT OR COBALT-CHROMIUM AS A BINDER FOR BOROLITE IV

Another attempt to effect a favorable change in the impact strength of Borolite IV was the substitution of cobalt, or a cobalt - chrome alloy, for all or part of the Cr-Mo binder.

##### 1. Cobalt-Chromium Alloy

A 70-30 cobalt - chromium alloy is commercially available as powder, and some of this material was purchased to be used as a binder for Cr<sub>2</sub>B. The



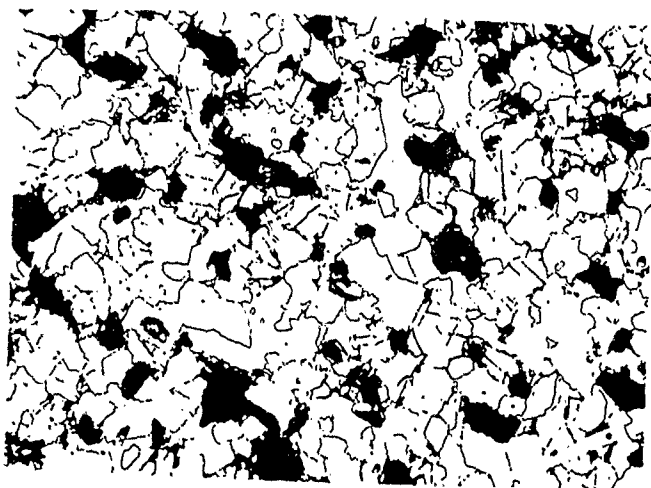


Fig. 11 Borolite IV 20/80  
+ 2% Cr<sub>2</sub>O<sub>3</sub>

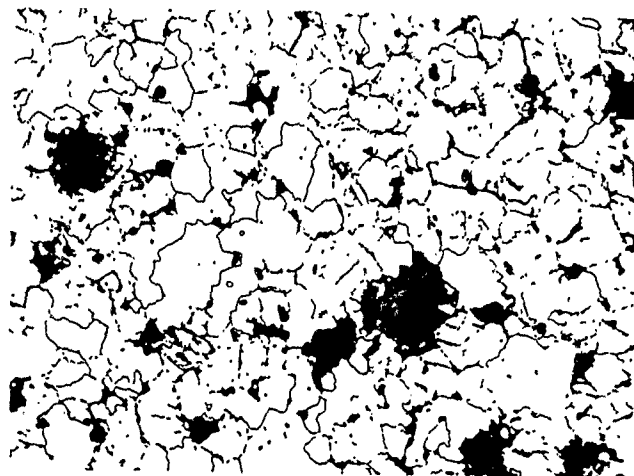


Fig. 12 Borolite IV 20/80  
+ 2% Ni

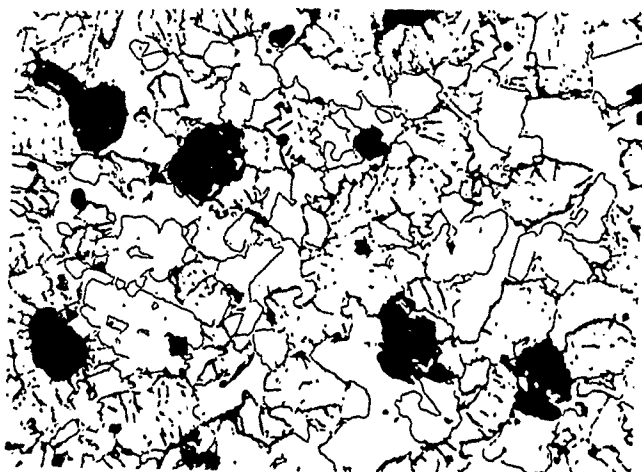


Fig. 13 Borolite IV 20/80  
+ 2% Cu

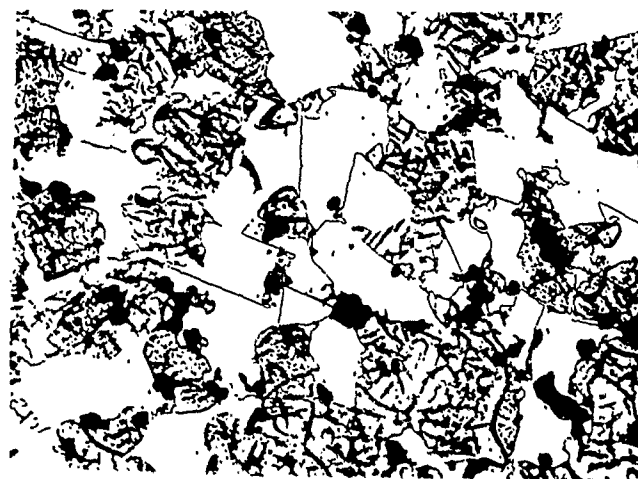


Fig. 14 Borolite IV 20/80  
+ 2% Ti

alloy analyzed only 65.5% Co and 29.1% Cr, with the rest unknown.

This alloy itself has a considerable impact strength and ductility. NACA drop impact tests on sintered bars showed a slight bend at 11 inch pounds, and little, if any, further effect at 30 inch pounds. Ballistic impact tests produced only dents in the samples at the highest firing pressures available.

The Co-Cr alloy itself, however, is too ductile for elevated temperature use. It was not possible, for example, to run a transverse rupture test at 1800°F--the bar would not break, but bent until both sides of the indenter were resting upon the specimen. A room temperature transverse rupture strength of 180,300 psi is excellent.

A photomicrograph of this transverse rupture test specimen is shown in Figure 15. This is one type of microstructure such as is being sought for Borolite IV; small amounts of liquid surrounding each individual grain of the major constituent.

## 2. Co-Cr As a Binder for Cr<sub>2</sub>B

With this ductile, impact resistant material available, one obvious experiment was to use it as a binder for Cr<sub>2</sub>B. The Co-Cr alloy sinters at 1320°C, so there was a possibility of a useful high temperature system.

The first such composition made was 20 Cr<sub>2</sub>B - 80 Co-Cr alloy. This material showed some impact strength, NACA drop impact tests varying from 4.5 to 11.0 inch pounds for specimens with about 0.200" square cross section. In ballistic impact tests, these specimens could just barely be broken at the highest firing pressure available, but they did not shatter.

Room temperature transverse rupture strengths were excellent, averaging 170000 psi. This strength decreased to an average of 143000 psi at

1600°F and a similar value at 1800°F. Maximum values were 188000 psi at room temperature and 168000 psi at 1800°F.

The sintering and hot pressing temperatures, however, were fairly low, just under 1200°C, and a bend test (40000 psi at 1800°F) produced a 0.028" deflection in 18 hours, which is much higher than for Borolite IV.

A stress-to-rupture test was run at 1800°F; however, the sample broke after a load equivalent to 13520 psi had been applied. In this test, a load of 8700 psi had been supported for 1/2 hour. At fracture, the specimen, which did not indicate any particular flaws, had an elongation of 3.5% and a reduction of area of 7.5%. This indicates a very high creep rate.

Three photomicrographs of samples of this material are shown in Figures 16 - 18. Figure 16 shows a transverse rupture specimen, hot pressed. Figure 17 shows a corresponding impact specimen, sintered. In each case, a eutectic structure is visible, with the hot pressed bar, as expected, indicating a finer structure. Figure 18 is a photomicrograph of a hot pressed impact bar of this same material. While the treatment was intended to be similar, it is possible that the particular type of hot pressing die used to make that specimen caused effectively a quench from the liquid, since there is no appearance of the eutectic structure. It is believed that this only indicates a lack of equilibrium in that sample.

Another set of experiments was conducted with a 5 Cr<sub>2</sub>B - 95 Co-Cr composition. These were started concurrently with the 20/80 compositions, before the low stress-to-rupture strength of the latter was known.

The results with this 5/95 composition were similar to those with 20/80; a good impact strength, good room temperature strength, but poor resistance to creep at elevated temperatures.

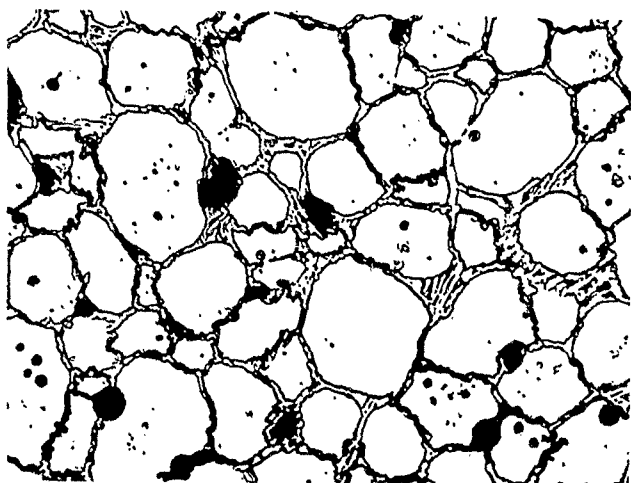


Fig. 15 Co-Cr 70/30

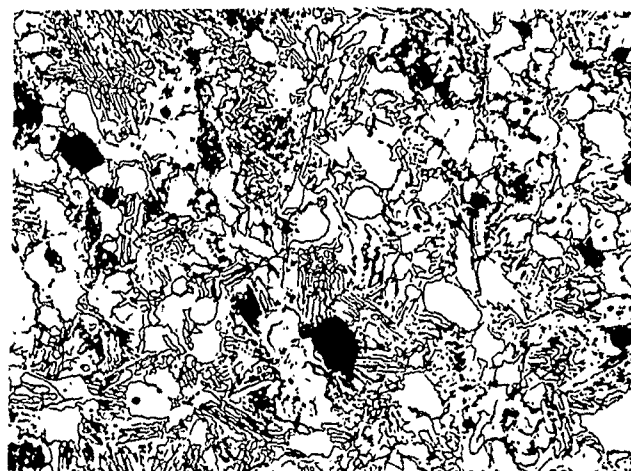


Fig. 16 20/80 Cr<sub>2</sub>B/Co-Cr  
Hot Pressed Transverse Bar



Fig. 17 20/80 Cr<sub>2</sub>B/Co-Cr  
Sintered

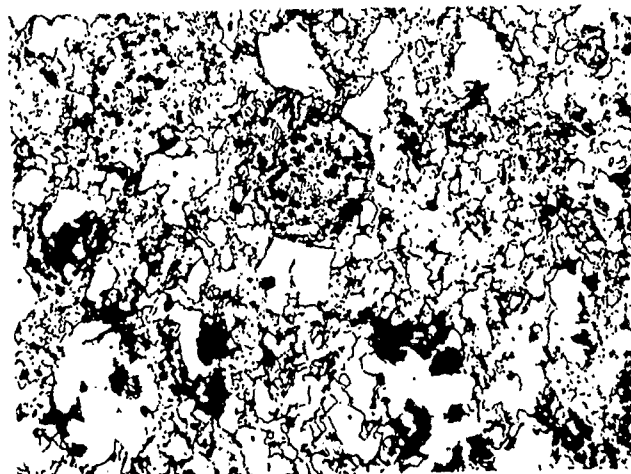


Fig. 18 20/80 Cr<sub>2</sub>B/Co-Cr  
Hot Pressed Impact Bar

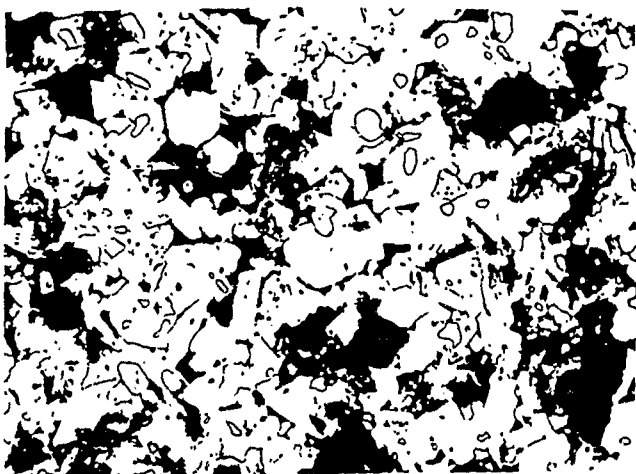


Fig. 19 84/16 Cr<sub>2</sub>B/Co

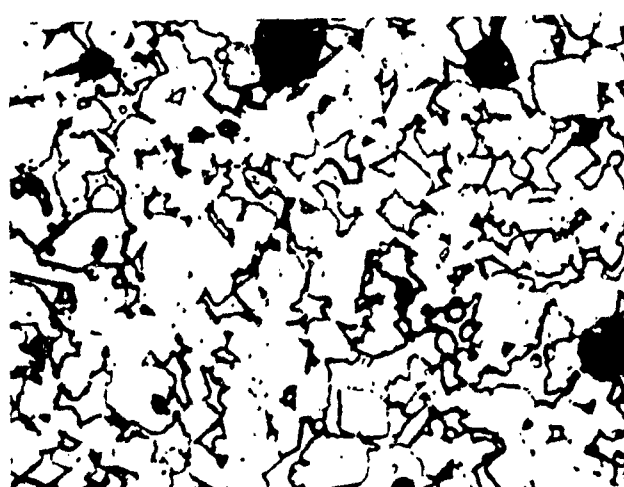


Fig. 20 50/50 Cr<sub>2</sub>B/Co

NACA drop impact strengths ranged from a break at 11 inch pounds to a bend at 14.8 inch pounds. Room temperature transverse rupture strength was 180700 psi, but this property could not be measured at 1800°F--the specimen bent to the limits of the setup without breaking.

In stress-to-rupture tests, one bar, dented at 1800°F, broke after a 12500 psi load was applied, with an elongation of 5.4% and a 12.3% reduction in area. A second test, at 10000 psi and 1800°F, had all the weight added at once. In this test, the bar hung for 1.3 hours, after which the fractured specimen showed a 4.9% elongation and a 13.6% reduction in area.

Still another stress-to-rupture test was run with this 5/95 Cr<sub>2</sub>B/Co-Cr material, at 5000 psi and 1800°F. Again, the entire load was applied at once, at temperature. This bar held for 17.6 hours, with an elongation of 3.5% and a 4.0% reduction of area.

### 3. Cr<sub>2</sub>B/Co-Cr/Mo

In an attempt to retain the impact strength added by the Co-Cr binder, while regaining some of the stress-to-rupture strength of Borolite IV, two batches were made of Cr<sub>2</sub>B, Co-Cr and Mo. The composition was:

Cr<sub>2</sub>B - 20% by weight

Co-Cr- 64% by weight

Mo - 16% by weight

This material was also sintered or hot-pressed in the temperature range 1150 - 1200°C. It showed excellent transverse rupture strength, both at room temperature and at 1000°C, in the range of 130000 psi cold and up to 159000 psi at 1000°C. In each case, the strength values for sintered pieces were about 25% higher than for hot pressed samples of similar density.

Impact strengths were measured in the NACA drop impact tester, on bars with approximately 0.200" square cross-section. The impact strength ranged from 2.2 to 5.4 inch pounds, again with the higher values for sintered bars.

Two hot bend tests, 40000 psi at 1800°F, gave very large deflections, one bar reaching the limit of the apparatus, 0.085", overnight, and the other deflecting 0.043" overnight. This is in the same general range as the Cr<sub>2</sub>B + Co-Cr compositions previously tested, so it appeared that the stress-to-rupture values at 1800°F would be in the same low range.

One photomicrograph was taken, of a sintered bar, but other than the fact that the individual particles were quite small, little detail could be determined.

#### 4. Cr<sub>2</sub>B + Co

As a part of the Co-Cr investigation, a few experiments were made with Cr<sub>2</sub>B - Co compositions.

With 16% Co, the sintering temperature dropped from the 1500°C needed for Borolite IV to 1400 - 1425°C. The transverse rupture strengths obtained were low, both at room temperature and at 1800°F, and the density of these pieces was not too good. There was more ductility than with Borolite IV as is shown by a comparison of the hot bend test results:

Borolite IV, deflection 0.004" in 24 hours

84 Cr<sub>2</sub>B + 16% Co, deflection 0.016" in 22 hours

However, an impact bar gave a result of only 0.7 inch pounds in the NACA drop impact test. The hardness was quite high, reaching 90 on the Rockwell A scale. Figure 19 shows a photomicrograph of one of these specimens, indicating the exceedingly large porosity.

Batches with 25 and 50% cobalt were also made. In both of these cases, the sintering temperatures dropped off considerably, being in the range of 1150°C, or even lower. This would indicate a reaction, probably involving cobalt and boron. Transverse rupture strengths were in the order of 70000 psi, both cold and at 1800°F; the hardness was RA 74 for the 25% Co and 78 - 81 for the 50% Co batch. Impact strengths were not measured.

A photomicrograph of 50/50 - Cr<sub>2</sub>B/Co is shown in Figure 20. Various etches failed to show up much detail--it is not clear whether there is actual porosity or another constituent around many of the grains. The overall density of the samples was 7.1 g/cc, probably not too far from the theoretical value.

One additional batch was made with 20% Co. This material, after heating in hydrogen in the high frequency setup, appeared to be quite tough and difficult to break down, like the 80-20 Cr-Mo alloy. However, impact bars made from this material showed only 1-2 inch pounds in the NACA drop test.

#### F. COATING

The idea of coating a strong but fairly brittle high temperature material with a material such as Inconel was not carried further during this report period.

It had been found that if the base material is very brittle, then an excessively thick coating is required in order to have any appreciable impact strength in the overall material. A very thick coat would defeat the purpose of having a strong and oxidation resistant material, and would restrict such a combination from many intended high-temperature applications.

For this reason, coating of Borolite IV or related materials is being held up until a material can be developed with both a high stress-to-rupture life and a somewhat larger impact strength than the present Borolite IV.

One coating attempt was made, however, Several Borolite IV 20/80 impact bars were sent to the Chromalloy Corporation to be chromized. It has not yet been possible to deposit a thick enough coating of chromium on these samples to improve the impact properties.

G. CONCLUSIONS AND FUTURE WORK

The investigations started during this report period actually require further work to come to a successful conclusion. The work has shown that it is possible to alter the microstructure of Borolite IV, though this has not yet been correlated with any changes in impact strength. Extension of this work to greater percentages of other materials than cobalt, and a more detailed study of sintering and heat treating conditions may be fruitful in this respect.

Very little has been done with respect to complete purification of Borolite IV -- the original improvement in the properties of Borolite IV caused by the partial purification of the Cr-Mo alloy in its preparation leads to the hope that this investigation may also be effective.

It has been found possible to make an impact resistant material from  $\text{Cr}_2\text{B}$  and a Co-Cr alloy, but this type of composition has not shown both impact strength and elevated temperature creep resistance properties. It may be possible to carry further the partial substitution of the Co-Cr and Cr-Mo alloys to try to retain the desirable qualities of each as a binder for  $\text{Cr}_2\text{B}$ .



### III BASIC RESEARCH

During this contract period, basic research was done on three different problems, one an attempt to find another type of high temperature material, the others more fundamental investigations relating to the understanding of borides. This work included:

The System Niobium - Boron;

New Borides of Yttrium and Rare Earth Metals:



Other Special Borides

Indium

Gallium

Much of this work was in the nature of an introductory exploration, with further continuation necessary later on.

#### A. SYSTEM Nb-B

A different type of high temperature material possibility would be a composition in the niobium - boron system. Although niobium metal is known to oxidize in air above 250°C, it forms a typical transition metal diboride which has fair oxidation resistance.

An investigation of the low boron end of the Nb-B system was initiated, up to a content of 3% boron. Niobium powder, -325 mesh, was obtained from Fansteel Metallurgical Corporation. A typical analysis of this material was as follows, as furnished by the supplier:

Nb	: 99.0%
C	: 0.5%
Ta	: 0.5%
Ti	: 0.04%
Fe	: 0.01%

The boron used in this investigation was grade "D" boron obtained from Cooper Metallurgical Associates. This powder analyzed as follows:

B	= 96.32%
C	= 0.26%
Fe	= 0.60%

These powders were reacted in ceramic boats, in tube furnaces, under hydrogen, since any contact with carbon or a carbonaceous atmosphere would lead to the formation of carbides.

The first run was made with 3% B, heated at 1300°C in a global-heated Lindberg furnace. The slug oxidized considerably upon removal from the furnace, and analyzed to only 88.9 Nb and 2.86 B. This run was repeated in a gas-fired Remmey furnace, at 1400°C, with a purified hydrogen atmosphere. Here the results were better, but the material still contained a considerable amount of impurities. Similar runs at 1450°C were also made with materials containing 1 and 0.5% B. The chemical analyses are given in Table I.

Table I - Analysis of First Nb-B Batches

Lot #	Original Boron Content	Nb	B	N	O	H
Nb-2	3 %	93.0	2.78	0.45	1.46	0.20
Nb-3	1 %	94.0	0.87	0.59	2.51	0.31
Nb-4	0.5%	95.0	0.43	0.69	1.82	0.30

These powders were crushed, ball milled, and used to make small rectangular test specimens, by hot pressing. The physical properties obtained from these samples are given in Table II.

Table II - Physical Properties of Test Specimens  
Made from First Nb-B Batches

Lot #	Density g/cc	Resistivity Microhm--cm	Transverse Rupture, PSI Room Temp.	Hardness Rockwell A
Nb-2	7.54	27.7	52700	88.3
Nb-3	7.80	37.5	65800	87.4
Nb-4	7.82	35.0	61100	83.4

These samples were analyzed chemically after hot-pressing. The results are given in Table III.

Table III - Analysis of Nb-B Samples after Hot-Pressing

Lot #	Nb	B	C	N	O
Nb-2	92.6	2.82	0.98	0.56	3.2
Nb-3	95.0	0.80	1.00	0.83	1.90
Nb-4	94.9	0.44	0.95	0.67	1.47

It can be noted that there is little change, other than carbon pickup, except for the considerable increase in oxygen content of Nb-2. Iron analyses, which would have indicated the pickup in crushing and milling, were not done.

Oxidation tests were run on these three materials, at 1800°F in still air. In one-half hour, very voluminous, non-adherent, yellow-white oxidation products had formed, in a Maltese cross pattern. The amount of weight gain for each sample was as follows:

Nb-2	+ 6.6 mg/cm <sup>2</sup>
Nb-3	+14.2 mg/cm <sup>2</sup>
Nb-4	+ 7.9 mg/cm <sup>2</sup>

each referring to 1/2 hour at 1800°F.

There was not enough of these materials to make impact tests, so a similar batch, with 3% boron, was made up for this purpose. Two bars with densities of 7.66 and 7.73, each 0.160" x 0.220", were tested in the NACA drop impact tester. The results were 1.1 and 1.3 inch pounds.

Believing that the lack of oxidation resistance and low impact strength might be closely allied with the impurity content, attempts were made to produce purer materials.

Batch Nb-6 was arc-melted in a vacuum system first evacuated and then filled with argon. This procedure, did not improve the total analysis, which was

Nb - 94.1 %      B - 2.65%      N - 0.30%      O - 2.36%

A second arc-melting run, after the system was checked for any possible leaks, was not any better, although this material was somewhat difficult to crush.

A hot pressed sample of the first arc-melted run, with a density of 7.77 g/cc, gave a value of 1.6 inch pounds in the NACA drop impact tester.

This piece, however, was very hard, indicating a value of 90 on the Rockwell A scale.

To make a material with a lower impurity content, a mixture of Nb powder and 1% boron, compressed into a small slug, was heated in a large vacuum furnace, evacuated and filled to a small pressure of argon.

This did not help at all, though the fact that this run was very long and interrupted may have led to the introduction of impurities. The analysis was:

B - 0.78%  
H - 0.0085%  
N - 0.284%  
O - 4.27%.

With this content of impurities it is not surprising that it was difficult to press sound pieces.

X-ray diffraction analysis was done on each powder, and the results agree with the chemical analyses and physical property results. In each case, there exists a cubic compound, with lattice parameter close to  $4.20 \text{ \AA}$ . This is in the range of a compound variously considered as a monoxide (NbO) or a mixed oxide-nitride.

The compositions containing 3 and 1% boron also show both NbB and a hexagonal  $\text{Nb}_x\text{B}_y$ , similar to the  $\text{Nb}_5\text{B}_3$  reported by Brewer.<sup>1</sup> The separate  $\text{Nb}_5\text{B}_3$ , also reported by Brewer, was not seen, although it is possible that this is due to the temperature ranges involved in the various studies.

The hexagonal boride, with lattice constants  $a \approx 6.18$  and  $c \approx 4.96 \text{ \AA}$ , resembles the tetragonal  $\text{M}_2\text{B}$  compositions in its dimensions, but is definitely not isomorphous with those compounds, even though the composition may be  $\text{Nb}_2\text{B}$ .

<sup>1</sup>Journ. Am. Cer. Soc. 34, 173, 1951

A shift in the lines of the NbB patterns of two of the hot pressed samples--Nb-2, Nb-3--may indicate a range of homogeneity for this compound. The presence of more than one niobium boride is an indication that equilibrium had not been reached, or that oxygen has a pronounced influence on the stability of these borides.

The composition containing 1/2 percent boron did not show any NbB, but only the cubic compound and the hexagonal  $Nb_xB_y$ . No evidence of any lower boron-containing compound was found.

It appears that the properties of Nb-B compositions will be dependent upon the content of impurities, and that to obtain a material which might be useful at elevated temperatures, the contents of nitrogen and oxygen, especially will have to be sharply reduced.

## B. BORIDES OF YTTRIUM AND RARE EARTH METALS.

### 1. Introduction

There has been a great deal of interest in metals of the rare earth group and their compounds in recent years. Considerable work has been done on rare earth borides, with several new rare earth borides having been discovered as a result of work on this contract.<sup>1</sup>

This work has now been extended to include an investigation of the borides of yttrium, the element occurring directly above lanthanum and the rare earth group in the periodic table. Though yttrium is not actually one of the rare earth metals, it often occurs with metals of this group, and exhibits similar physical and chemical behavior.

<sup>1</sup> B. Post, D. Moskowitz and F. W. Glaser - J. A. C. S. 78, 1800, 1956

## 2. Raw Materials and Procedure

Yttrium oxide powder, 99.9% pure, was obtained from A. D. Mackay, Inc. as a starting material for this investigation. Borides were formed from the oxide by heating with boron and carbon, in a fashion similar to that previously used for the rare earth metals. Boron with an analysis 96.32% B, from Cooper Metallurgical Associates, was used as the source of boron.

The oxide, boron and carbon were thoroughly mixed, pressed to form small slugs, and heated in a hydrogen atmosphere, either in carbon crucibles in a high frequency setup, or in ceramic boats in a gas-fired tube furnace.

## 3. New Borides

The only yttrium boride previously known was  $YB_6$ , reported over 25 years ago.<sup>2</sup> Because of the similarity of yttrium to the rare-earth group, it was expected that there would also be a tetraboride.

This new compound,  $YB_4$ , was immediately found. Heating mixtures of  $Y_2O_3$ , B and C to temperatures of 1400 to 1800°C, either in graphite crucibles or in ceramic boats,  $YB_4$  was easily produced, not completely pure, but as a definite major constituent.  $YB_4$  is isomorphous with the tetraborides of the rare earth metals. It is tetragonal, with lattice parameters  $a = 7.091$ ,  $c = 4.014 \text{ \AA}$ ,  $c/a = 0.558$ . A list of the observed 2 $\theta$  reflections for the X-ray diffraction pattern of this compound is given in Table IV, along with the  $d$  spacings, observed relative line intensities and  $hkl$  indices.

Still following the pattern of the rare earth metals, yttrium was found to form another new boride,  $YB_x$ , isomorphous with the rare earth  $MB_x$  compounds.<sup>1</sup> In this case,  $x$  is believed to be 3, and there are indications that in the case of yttrium,  $YB_x$  is formed only at quite high temperatures.

<sup>2</sup> L. Andrieux, Ann. Chim., 12, 423, 1929

TABLE IV  
X-RAY DATA FOR YB<sub>4</sub>

2θ Cu K <sub>α</sub>	d	I	hkl
22.15	4.0096	42	001
25.15	3.5379	42	200
28.15	3.1673	69	210
33.75	2.6535	57	201
35.8	2.5060	15	220
36.1	2.4859	100	211
40.25	2.2387	24	310
42.5	2.1252	18	221
45.15	2.0064	24	002
46.1	1.9673	3	320
46.4	1.9552	21	311
51.8	1.7634	6	321
52.35	1.7461	12	202
53.25	1.7187	27	410
54.1	1.6937	21	212
54.9	1.6709	18	330
58.3	1.5813	27	411
59.85	1.5440	15	331
62.0	1.4955	6	312
65.8	1.4180	9	430

Tetragonal       $a = 7.09_{-1}^{+0} \text{ \AA}$   
 $c = 4.01_{-4}^{+1} \text{ \AA}$



Strangely enough, the  $YB_6$  compound did not form at all readily under the conditions used here.

$YB_x$  is also tetragonal, with  $a = 3.78$ ,  $c = 3.55 \text{ \AA}$ ,  $c/a = 0.94$ . This compound also was always produced with at least one other boride present. This, and the usual presence of some oxide and carbon in the final products, made it impossible to prove definitely that  $YB_x$  is  $YB_3$  by chemical analysis. Table V gives the x-ray diffraction data for  $YB_x$ .

Up to this point, while new compounds had been discovered, they had all been similar to previously known borides, such as those of cerium, thorium and other rare earths. However, attempting to make lower boron-containing borides than  $YB_4$  or  $YB_x$  produced quite different results. At least one definite new boride was formed, and there are possibly two or three more compounds in the system, as yet not resolved.

The new boride was first found by a low temperature ( $1200^\circ\text{C}$ ) long time heating of a product which was essentially  $YB_4$ . In the course of this heating, the material lost boron, partly oxidized, and transformed completely. After 16 hours, no  $YB_4$  remained; instead, in addition to some  $Y_2O_3$ , there were now two new hexagonal compounds.

Reheating several other batches, originally containing either  $YB_4$  or  $YB_x$ , or both, in the range of  $1170$  to  $1300^\circ\text{C}$ , produced in each case the first of these hexagonal compounds. Also, starting with a mixture designed to produce " $YB_2$ ", the same compound was formed as the major constituent. In all cases after the first one,  $YB_4$  was also present, sometimes with additional, as yet unexplained, lines in the x-ray diffraction pattern. Also, in some cases,  $YB_x$  occurred with this new compound.

TABLE V  
X-RAY DATA FOR YB<sub>x</sub>

2θ Cu Kα	d	I	hkl
23.6	3.7666	32	100
25.05	3.5517		001
33.55	2.6688	16	110
34.65	2.5866	43	101
48.15	1.8882	9	200
51.4	1.7762	7	002
54.25	1.6894	10	210
55.05	1.6667	8	201
57.2	1.6091	6	102
60.65	1.5256	7	211
62.8	1.4784	4	112

Tetragonal     $a = 3.78 \text{ \AA}$   
                   $c = 3.55 \text{ \AA}$

Identification by chemical analysis was difficult. In addition to the fact that the new compound normally occurred with other borides, small amounts of carbon and some oxide, new methods of analysis had to be developed, slightly varied from previous standard methods for determining yttrium.

The best determination, therefore, seemed to be by x-ray diffraction. The compound is hexagonal, with  $a = 3.78$  and  $c = 4.40 \text{ \AA}$ ,  $c/a = 1.16$ . This is similar to the hexagonal diborides of the transition metals of the fourth to sixth groups; the cell is larger and the  $c/a$  ratio much greater. However, the  $c/a$  ratio is quite similar to that of  $\text{MgB}_2$ , and in similar fashion, yttrium is a rather large atom.

It is, therefore, postulated that this new compound is a  $\text{YB}_2$ , in which the larger size of the yttrium atoms expands the "normal"  $\text{MB}_2$  lattice of the transition metal diboride type.

This large expansion, in the "c" direction, may account for the fact that this diboride does not appear to be stable at temperatures much above  $1300^\circ\text{C}$ . At higher temperatures, the  $\text{B}_2$  appears to transform into the  $\text{B}_x$  structure, which might have a large enough homogeneity range. This seems possible, since the a dimension of the  $\text{YB}_2$  and  $\text{YB}_x$  lattices is the same. Observed x-ray data for  $\text{YB}_2$  are given in Table VI.

The other hexagonal compound has not been found in later batches, so it is not known whether this was a boride, or some compound containing or stabilized by oxygen or carbon.

Other x-ray patterns appear to exist in this system, especially in the region with low boron content, but no other definite compounds have yet been determined.

TABLE VI  
X-RAY DATA FOR YB<sub>2</sub>

$2\theta$ Cu K $\alpha$	d	hkl
20.15	4.4030	001
27.2	3.2757	100
34.1	2.6270	101
40.95	2.2020	002
48.1	1.8900	110
49.9	1.8260	102
52.65	1.7369	111
56.1	1.6380	200
60.3	1.5335	201
63.2	1.4700	003
65.0	1.4336	112

hexagonal       $a = 3.78 \text{ \AA}$   
 $c = 4.40 \text{ \AA}$        $c/a = 1.16$

#### 4. SmB<sub>2</sub>

With the demonstrated similarity between yttrium and the rare earth metals, it was then attempted to form a boride similar to YB<sub>2</sub> with a rare earth. Samarium was chosen for this attempt, using very pure Sm<sub>2</sub>O<sub>3</sub> on loan from The Ames Laboratory of Iowa State College.

Previous attempts had been made to form a samarium boride in the range of "SmB<sub>2</sub>" or "SmB", but these had all failed. It now appears that one reason for this failure was the fact that all such runs were made in the temperature range of 1700 - 1800°C.

A mixture of Sm<sub>2</sub>O<sub>3</sub>, B and C in a ratio to produce "SmB<sub>2</sub>", was heated at 1150°C. The x-ray diffraction pattern of the product showed two phases, the well-known SmB<sub>6</sub>, and a hexagonal compound with lattice parameters  $a = 3.86$ ,  $c = 4.48 \text{ \AA}$ ,  $c/a = 1.162$ , very similar to the YB<sub>2</sub> lattice. Since the analysis of samarium and boron totalled close to 90%, it is a good assumption that this compound also is a diboride, SmB<sub>2</sub>. The x-ray data for this compound is listed in Table VII.

Samarium is also a rather large atom, which would expand the "normal" transition metal diboride structure. The SmB<sub>2</sub> structure seems to be such, that strictly from geometrical considerations, the boron atom acts as though it has an effective radius of  $1.22 \text{ \AA}$ , considerably larger than in any of the transition metal boride structures.

#### 5. YbB<sub>2</sub>

Another attempt was made to form a rare earth diboride, this time using ytterbium oxide. This very pure Yb<sub>2</sub>O<sub>3</sub> was also obtained on loan from the Ames Laboratories of Iowa State College.

Here, too, previous attempts to make a lower boron containing ytterbium boride than YbB<sub>4</sub> or YbB<sub>x</sub> had failed, due to the high temperatures of operation. Yb<sub>2</sub>O<sub>3</sub>, B and C in the Yb/B ratio 1/2 were heated at 1190°C. The products contained Yb<sub>2</sub>O<sub>3</sub>, YbB<sub>6</sub>, and a hexagonal phase,  $a = 3.72$  and  $c = 4.35 \text{ \AA}$ ,  $c/a = 1.17$ . This gives a structure very similar to that already found in YB<sub>2</sub> and SmB<sub>2</sub>. It is possible to conclude that the ytterbium - boron

TABLE VII  
X-RAY DATA FOR  $\text{SmB}_2$

$2\theta$ Cu $K_{\alpha}$	d	hkl
26.6	3.3482	100
33.4	2.6804	101
40.2	2.2413	002
47.0	1.9317	110
49.0	1.8574	102
51.4	1.7762	111
54.8	1.6737	200
58.8	1.5690	201
63.5	1.4638	112

hexagonal     $a = 3.86 \text{ \AA}$   
                   $c = 4.48 \text{ \AA}$      $c/a = 1.162$

system includes a compound other than  $\text{YbB}_6$ ,  $\text{YbB}_4$  and  $\text{YbB}_x$  that this compound is of the same form as the  $\text{YB}_2$  and  $\text{SmB}_2$  structure, and that it is also probably a diboride.

#### C. OTHER SPECIAL BORIDES

Knowing that magnesium and aluminum form borides ( $\text{MgB}_2$  and  $\text{AlB}_2$ ), a few attempts were also made to produce borides of group IIIB metals.

Gallium and indium are quite similar to aluminum, chemically, and compounds similar to  $\text{AlB}_2$  might be possible. Gallium oxide, 99.8% pure, was obtained from A. D. Mackay, Inc. and indium metal powder from the Indium Corporation of America.

No positive results were obtained from heating indium with boron, but a mixture of  $\text{Ga}_2\text{O}_3$ , B and C produced a cubic x-ray pattern not related to any known carbide, oxide or other known compound of gallium. No chemical analysis has yet been done on this material, but it is possible that it is a boride.

#### D. PUBLICATIONS

During the past year, three publications based upon this contract appeared in print:

B. Post, D. Moskowitz, F. W. Glaser  
"Borides of Rare Earth Metals"  
J.A.C.S., 78, 1800, 1956

D. Moskowitz  
"A New Vanadium Boride of the Composition  $\text{V}_3\text{B}_4$ "  
Journal of Metals, in print

I. Binder  
"New Borides of Yttrium"  
Powder Metallurgy Bulletin, 7, 74, 1956

Reprints of the first and the last are bound into this report

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## Borides of Rare Earth Metals

By B. POST, D. MOSKOWITZ<sup>1</sup> AND F. W. GLASER

RECEIVED OCTOBER 29, 1955

Until recently, hexaborides were the only binary compounds known to be formed between rare earth metals and boron. In this study, a series of tetragonal tetraborides of Pr, Sm, Gd and Yb isomorphous with CeB<sub>4</sub>, ThB<sub>4</sub> and UB<sub>4</sub> were prepared and their lattice constants measured. The hexaborides of the above rare earth metals, as well as those of La and Th, were also prepared by carbon and boron reduction of their respective oxides. In addition, a group of isomorphous borides of a hitherto unreported structural type were found. The exact boron content of these compounds has not yet been determined.

### I. Introduction

A wide variety of binary compounds are formed between boron and the transition metals of the 4th, 5th and 6th groups of the Periodic Table. These range in composition from M<sub>2</sub>B to MB<sub>12</sub>.<sup>2</sup> No such variety, however, characterizes the compounds formed between boron and the rare earth metals. Rare earth metal borides of the type MB<sub>6</sub> were prepared and described many years ago,<sup>3,4</sup> and, until recently, no other rare earth borides were known. Within the past few years, however, three compounds of the type MB<sub>4</sub> were prepared<sup>5-8</sup>; of these, one, CeB<sub>4</sub>, is a rare earth metal boride and the other two (UB<sub>4</sub> and ThB<sub>4</sub>) are closely related.

One of the objectives of the present investigation was the preparation and the study of hexaborides of various rare earth metals and of tetraborides of rare earth metals other than Ce. Efforts also have been made to prepare binary boride phases other than MB<sub>6</sub> or MB<sub>4</sub>. In addition, procedures have been studied for the preparation of such binary borides by the direct reduction of the metal oxides by boron.

### II. Raw Materials

Sm<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> were obtained from the Ames Laboratory of Iowa State College. The samarium and gadolinium oxides were of a purity greater than 99.9%, while the ytterbium oxide was 99.7% pure. The "Pr<sub>2</sub>O<sub>3</sub>" used was of a minimum purity of 93/94%, and contained about 5% La<sub>2</sub>O<sub>3</sub>. The La<sub>2</sub>O<sub>3</sub> was of two grades, one of about 92% minimum purity, and the other approximately 99% pure. The boron powder used, purchased from Cooper Metallurgical Associates, was 96.3% pure, and contained 0.60% Fe and 0.26% C. The carbon used was Fisher carbon black "G" (gasblack).

### III. Preparative Methods

Small amounts of rare earth oxide, boron and carbon black powders (totaling about 1 g.) were hand-mixed in the desired proportions until homogeneous and pressed at about 5 t.s.i. into thin wafers (1" × 1/2" × 1/16"). These were separately loaded into graphite crucibles about 1.5" high by 5/8" in diameter. The latter were in turn placed in larger graphite crucibles (4" × 3") and heated by induction in a hydrogen atmosphere; specimens were heated either for 2 hours at 1500° or for 1 hour at 1800°.

(1) To whom inquiries may be addressed.

(2) R. Kiessling, *Acta Chem. Scand.*, **4**, 209 (1950).

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After heating, the sintered compacts were crushed to a fine powder and analyzed chemically and by X-ray diffraction methods to determine the reaction products.

There were strong indications that, especially in reactions carried out at 1800°, the boron, rather than the carbon, acted as the reducing agent. When no carbon was added to the reaction mixtures (enough excess boron was added to reduce the oxide by forming the volatile B<sub>2</sub>O<sub>3</sub>), the borides readily were formed both at 1500 and 1800°. In the latter case, although no carbon was added to the reaction mixture, about 1 to 2% was picked up from the graphite crucibles. It was found that the borides were formed equally well in the absence of carbon, *i.e.*, where ZrB<sub>2</sub> crucibles were used as containers.

### IV. Experimental Results

a. Hexaborides (MB<sub>6</sub>).—The MB<sub>6</sub> phase appears to be by far the most stable of the rare earth borides. In all instances, when the appropriate amounts of boron and metal were caused to react, the MB<sub>6</sub> phase was formed. It was also detectable on most X-ray diagrams when other compositions were employed.

The hexaborides of the rare earth metals have been investigated extensively. The structure is of the CsCl type, *i.e.*, the unit cell is primitive cubic, with boron octahedra at the corners and a metal

TABLE I  
LATTICE CONSTANTS (IN Å.) OF THE CUBIC UNIT CELLS OF  
THE HEXABORIDES OF VARIOUS METALS

Metal	(1) <sup>a</sup>	(2) <sup>b</sup>	(3) <sup>c</sup>
Ba	4.29	4.268	
Sr	4.20	4.198	
Ca	4.153	4.145	
Y	4.08	4.113	
La	4.153	4.157	4.153
Ce	4.137	4.141	
Pr	4.129		4.130
Nd	4.126	4.128	
Sm			4.129
Eu			
Gd	4.13	4.112	4.110
Tb			
Dy			
Ho			
Er	4.11		
Tm			
Yb	4.14	4.144	4.140
Lu			
Th	4.16	4.113	4.110

<sup>a</sup> Various authors quoted in Kiessling.<sup>2</sup> <sup>b</sup> Blum and Bertaut.<sup>6</sup> <sup>c</sup> The present work.

atom at the body center of each unit cell. The lattice constants of the unit cells of hexaborides and related metals, as determined by various investigators, are listed in Table I.

In general, results obtained in the course of the present investigation agree well with those reported by Blum and Bertaut.<sup>6</sup> It is clear that the value of 3.16 Å. reported by Allard<sup>3</sup> for ThB<sub>6</sub> is considerably in error; Blum and Bertaut found the lattice dimension to be 4.113 Å.; in the present investigation it was found to be 4.110 Å.

The preparation of SmB<sub>6</sub> had not been reported prior to the present work; the lattice dimensions of this compound are of the expected magnitude.

**b. Dodecaborides (MB<sub>12</sub>).—**Dodecaborides of uranium<sup>9</sup> and zirconium<sup>10</sup> recently have been prepared and described. Efforts were made to prepare rare earth borides with this interesting crystal structure. In all cases, no phase richer in boron than MB<sub>6</sub> was detected in the X-ray diagrams when mixtures of composition MB<sub>12</sub> were prepared. Nor was any evidence of unreacted boron detected in the X-ray patterns. This did not necessarily imply that free boron was absent from the reaction products. The scattering power of boron is extremely low relative to that of the rare earth metals; some free boron might very well, therefore, have gone undetected.

In the case of Yb and La, when excess boron was used in the reaction (*i.e.*, when sufficient boron was used to form MB<sub>12</sub>), the MB<sub>6</sub> unit cell which was formed was very slightly smaller than in instances where the MB<sub>6</sub> phase was prepared using stoichiometric quantities of boron. It appears likely that the MB<sub>6</sub> structures in these cases contained large numbers of metal atom vacancies, since the actual composition was close to MB<sub>12</sub>, resulting in a diminution of the lattice constant. The absence of boron lines from the X-ray diagram of the reaction products is less puzzling in terms of this hypothesis.

In this connection, we may note that, in his detailed study of the thermionic properties of various metal hexaborides, Lafferty<sup>11</sup> has discussed the effects of migration of metal atoms through the boron lattice to cathode surfaces. He concluded that in the case of LaB<sub>6</sub>, "lanthanum diffuses out through the boron framework and evaporates, while the boron structure remains intact. After prolonged operation at high temperatures, the LaB<sub>6</sub> will become so depleted in lanthanum that the boron framework will collapse, leaving a boron coating on the cathode." The effect noted in the present study, if real, is quite consistent with Lafferty's hypothesis.

**c. Tetraborides (MB<sub>4</sub>).—**Brewer, *et al.*,<sup>5</sup> have described the preparation of UB<sub>4</sub>, ThB<sub>4</sub> and CeB<sub>4</sub>. The isomorphous structures of these compounds were determined by Zalkin and Templeton<sup>7</sup>; the unit cells are tetragonal with four formula weights per cell. Bertaut and Blum<sup>8</sup> have also prepared UB<sub>4</sub> and described its structure.

It appeared probable that other rare earth metals, in addition to Ce, form MB<sub>4</sub> phases, and that

the failure of previous investigators to detect this phase might very well have been due to the relatively low reaction temperatures employed in their preparation.

This expectation was realized. MB<sub>4</sub> phases, isomorphous with the structure reported by Zalkin and Templeton, and by Bertaut and Blum, were readily prepared. In no case, however, could a "pure" MB<sub>4</sub> phase be prepared; the X-ray diagrams always showed the presence in the reaction products of either MB<sub>6</sub> or a phase tentatively labelled MB<sub>x</sub>, in addition to the MB<sub>4</sub> compound. For reasons which are not at all clear, La, which readily formed LaB<sub>6</sub>, did not form detectable amounts of LaB<sub>4</sub>.

Lattice constants of CeB<sub>4</sub>, ThB<sub>4</sub> and UB<sub>4</sub>, as determined by Zalkin and Templeton,<sup>7</sup> are listed in Table II together with corresponding values for PrB<sub>4</sub>, SmB<sub>4</sub>, GdB<sub>4</sub> and YbB<sub>4</sub>, determined in the present investigation.

TABLE II

LATTICE DIMENSIONS OF MB<sub>4</sub> COMPOUNDS (Å.) (TETRAGONAL)

	<i>a</i>	<i>c</i>
CeB <sub>4</sub> <sup>a</sup>	7.205	4.090
ThB <sub>4</sub> <sup>a</sup>	7.256	4.113
UB <sub>4</sub> <sup>a</sup>	7.075	3.975
PrB <sub>4</sub> <sup>b</sup>	7.20	4.11
SmB <sub>4</sub> <sup>b</sup>	7.12	4.07
GdB <sub>4</sub> <sup>b</sup>	7.12	4.05
YbB <sub>4</sub> <sup>b</sup>	7.01	4.00

<sup>a</sup> Zalkin and Templeton.<sup>7</sup> <sup>b</sup> The present work.

**d. MB<sub>x</sub> Phase.—**In addition to MB<sub>6</sub> and MB<sub>4</sub> phases, lines of another, hitherto unreported, boride phase appeared in the X-ray diagrams, usually in addition to those of the other two phases (MB<sub>6</sub> and MB<sub>4</sub>). Although there were some indications of the presence of this "MB<sub>x</sub>" phase in patterns of borides of samarium, a definite identification could not be made in that case. In the cases of lanthanum, praeodymium, gadolinium and ytterbium, the additional phase could be identified readily. Each of these MB<sub>x</sub> phases contains one metal atom per unit cell; their unit cell dimensions are listed in Table III.

TABLE III

LATTICE DIMENSIONS OF MB<sub>x</sub> (Å.)

	<i>a</i>	<i>c</i>	Crystal system
LaB <sub>x</sub>	3.82	3.96	Tetragonal
PrB <sub>x</sub>	3.81	..	Cubic or pseudo-cubic
GdB <sub>x</sub>	3.79	3.63	Tetragonal
YbB <sub>x</sub>	3.77	3.56	Tetragonal

It was not possible to identify the compositions of these phases unequivocally by the usual analytical means. These compounds could be prepared reproducibly, and the constancy of the lattice dimensions—despite a variety of preparative methods—indicated that they possessed narrow ranges of homogeneity. The value of *x* is probably either 3 or 4. The possibility of stabilization of this phase by carbon could not be excluded, although the amount of carbon contained in the structure would have to be rather small. This was shown by

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(11) J. M. Lafferty, *J. Appl. Phys.*, **22**, 299 (1951).

the value of the lattice parameters which fit very well the atomic size of boron, and by chemical analysis.

A closer study of the dimensions of the  $MB_x$  compounds ( $LaB_x$ ,  $PrB_x$ ,  $GdB_x$ ,  $YbB_x$ ) reveals an interesting variation with atomic number.  $LaB_x$  is tetragonal, with "c" greater than "a" (3.96 versus 3.82 Å.).  $PrB_x$  is "cubic" with  $a_0 = 3.81$  Å.  $GdB_x$  and  $YbB_x$  are both tetragonal, but in their unit cells "a" is greater than "c." It is believed that all four compounds are really tetragonal and that they differ primarily with respect to axial ratios.  $c/a$  decreases from 1.036 in the case of  $LaB_x$ , to 1.000 in the case of  $PrB_x$ , to 0.962 for  $GdB_x$ , and 0.943 for  $YbB_x$ . If this view is valid, then  $PrB_x$  is only pseudo-cubic and should manifest its non-cubic character by splitting of lines on X-ray diagrams at elevated temperatures. This would result from dif-

ferences in coefficients of expansion in the "a" and "c" directions, if the compound is really tetragonal.

### V. Discussion

A careful X-ray study of the effective atomic sizes of the rare earth elements was carried out by Klemm and Bommer.<sup>12</sup> They found that, with the exception of Eu and Yb, these elements showed a regular decrease in atomic size as we proceed from La to Lu. The atomic radii of the two exceptions, Eu and Yb, are about 10% above the "normal" curve that may be drawn for the other rare earth elements (Fig. 1). These anomalies are associated with the abnormal valencies of these metal atoms; while most of the rare earth metals are essentially trivalent, Eu and Yb show a large amount of divalent character. The withdrawal of one electron from the outermost orbit to fill a gap in an inner one results in the observed increased sizes of these atoms.

The dimensions of the cubic  $MB_6$  unit cells (Table I) show a similar, though less pronounced, anomaly in the case of  $YbB_6$ , as shown in Fig. 1 (Eu $B_6$  has not yet been prepared).

It appears, therefore, that the effective valence state of the rare earth metals in the  $MB_6$  compounds is very much like that of the uncombined metals.

The ionic sizes of the rare earth metals ( $M^{+++}$ ) show no anomalies comparable to the above. The ionic radii of the trivalent rare earth ions decrease regularly from  $La^{+++}$  (1.061 Å.) to  $Lu^{+++}$  (0.848 Å.).<sup>13</sup> The lattice dimensions of the various  $MB_4$  and  $MB_x$  compounds listed in Tables II and III, respectively, also show a regular diminution with increasing atomic number of the metal.

A distinction may, therefore, be drawn between the relatively "metallic" character of the metal atoms in the  $MB_6$  compounds and their relatively "ionic" character in the  $MB_4$  and  $MB_x$  compounds.

Measurements of electrical conductivity, Hall constant, etc., should furnish critical tests of the above hypotheses.

YONKERS, N. Y.

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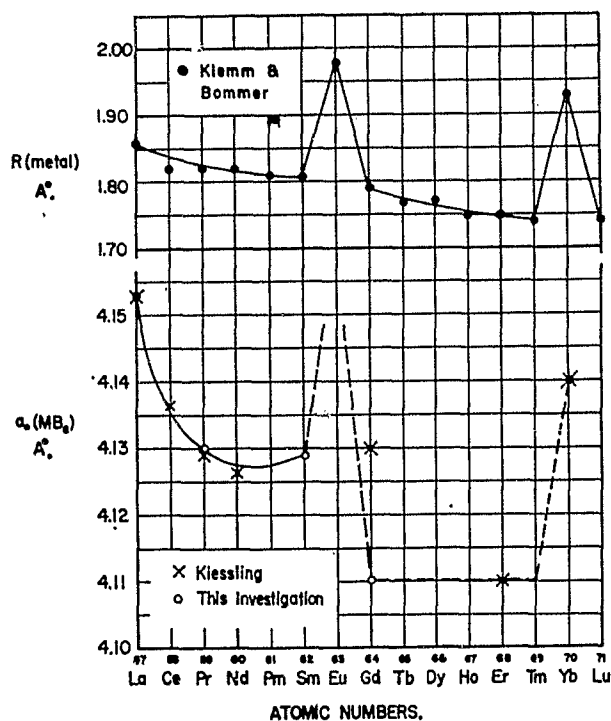


Fig. 1.—Atomic radii of rare earth metals and lattice parameters of rare earth hexaborides versus atomic number.

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*I. Binder*

NEW BORIDES OF YTTRIUM

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## NEW BORIDES OF YTTRIUM

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During the past few years, there has developed an ever increasing interest in the rare earth elements and their compounds. Some of this attention has also been focused upon yttrium, the element occurring directly above lanthanum and the rare earth group in the periodic table.

Rare earth borides of the type  $MB_6$ , were prepared many years ago.<sup>1, 2</sup> Until recently, these hexaborides were believed to be the only binary compounds formed between rare earth metals and boron. However, a few years ago, several borides of the form  $MeB_4$  were prepared. This group included one rare earth boride,  $CeB_4$ . More recently, in the course of a basic investigation of borides sponsored by ONR, other borides of several of the rare earth metals were made and identified.<sup>3</sup> Since yttrium, though not actually part of the rare earth group, occurs with and exhibits behavior similar to the elements in this group, it appeared logical to expect similar borides of yttrium.

$YB_6$  has been known for over 25 years,<sup>1, 2</sup> but no other Y borides were known until the present investigation. Two new yttrium borides, isomorphous with the recently found rare earth boride phases, have been discovered, and X-ray evidence indicates at least one additional boride and possibly still more in the Y-B system.

99+%  $Y_2O_3$ , obtained from A. D. Mackay, Inc., was used as the starting material, and various compositions were made by either carbon reduction or boron reduction, at temperatures from 1200° to 1800°C.

One of the new borides formed is  $YB_4$ , which has the tetragonal "ThB<sub>4</sub> type structure" determined by Zalkin and Templeton.<sup>4</sup> Lattice parameters are  $a=7.09$ ,  $c=4.01$ Å.

The second new yttrium boride definitely identified is  $YB_x$ , isomorphous with the  $LaB_x$ ,  $SmB_x$ ,  $PrB_x$ ,  $GdB_x$  and  $YbB_x$  recently reported.<sup>3</sup> The structure is tetragonal, with lattice parameters  $a=3.78$  and  $c=3.55$ Å, and the value of  $x$  is believed to be 3.

No boride with a boron content greater than  $YB_6$  has been found, consistent with the similar results obtained with the rare earth metals. On the other hand, compositions containing considerably smaller amounts of boron than  $YB_4$  gave at least two other x-ray diffraction patterns. One indicates a hexagonal unit cell, with  $a=3.78$  and  $c=4.40$ Å. This is somewhat similar to the diboride structure common to the transition metals. It is possible that the comparatively large atomic radius of yttrium, much larger than the atomic radius of any of the metals of groups IV through VI, causes a slight distortion of the normal  $MB_2$  structure. In fact,

the c/a ratio of this compound, 1.16, is closest to that of  $MgB_2$  (1.14) among the diborides, and magnesium also has a fairly large atomic radius.

So far, this hexagonal yttrium boride, and what is believed to be another hexagonal yttrium boride of another type, have only been made in combination with other Y borides, so that conclusive identification by chemical analysis has not yet been possible.

The author would like to acknowledge the cooperation of the Office of Naval Research, under whose sponsorship the current investigation was conducted.

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